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Chlorinated Solvent Decision Tree

DRAFT

For Groundwater Remediation

Division of Site Assessment, Remediation, and Revitalization

CHLORINATED SOLVENT DECISION TREE
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Chlorinated Solvent Decision Tree Introduction

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PURPOSE

The purpose of the Chlorinated Solvent Decision Tree is to improve remedial alternative selection for chlorinated solvents based on predicted effectiveness and desired remediation time frames. This document is focused on remediation rather than containment. For this reason, pump and treat was not included within the decision tree. Technologies that were included in this decision tree have been used successfully to treat chlorinated solvents at a number of sites across the state. For the purpose of this document, "chlorinated solvents" are limited to perchloroethylene (PCE), trichloroethylene (TCE), and degradation products including cis-1,2-dichloroethylene (cis-DCE), and vinyl chloride (VC). This document may be updated as new technologies are developed and shown to be successful at South Carolina chlorinated solvent sites and when sufficient information becomes available to assess strengths and weaknesses of the new technology.

INTENDED USE

The Chlorinated Solvent Decision Tree is a tool and is not to be used as a regulation. Existing regulations may prohibit the use of some of these technologies, and at some sites, site specific conditions may require selection of a technology not recommended or covered by this decision tree. Furthermore, this document does not attempt to address the more challenging issues associated with remediation of DNAPL source areas and/or contamination within fractured rock, although several of these remedial methods have been used successfully to treat areas where DNAPL was suspected to be present, and some of these technologies have been used in fractured rock.

GENERAL STRUCTURE

The document is divided into segments based on the desired remediation time frame given the known groundwater quality including concentrations of chlorinated solvents as well as general geochemical parameters such as ORP, pH, Sulfate, and Nitrate. It is possible that different portions of the plume may exhibit variable redox geochemistry such that more than one technology may need to be implemented to achieve remedial goals. Another likely scenario would be that one technology may be appropriate for the more concentrated portion of the plume and a second technology would be more appropriate for the distal part of the plume. Although the decision tree does not discuss these possible rationales for treatment trains, the decision tree may be used to develop a treatment train for a geochemically or spatially complex area of groundwater contamination.

Within the decision tree, chlorinated solvent plumes are divided into three categories: those that are more than 1000 times higher than the MCL or other standard; those that are between 50 and 1000 times the standard; and those that are less than 50 times the goal. At most sites, concentrations vary spatially; it is best to select a value that most closely reflects the majority of the plume, or, as discussed above, the plume may be subdivided into different portions based on concentrations, and differing technologies may be applied depending on the desired remediation timeframe. Consideration may also be given to the

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overall size of the plume; if a single well shows a significant impact, the decision tree may not be applicable.

Another separation of technologies is based on the ambient aquifer geochemistry. Again, the given ORP, pH, nitrate, and sulfate concentrations/ranges for a particular site should be the typical or predominant measurement based on groundwater quality evaluation. Averaging should not be performed to obtain a representative concentration. Rather, the most common concentration/range of sulfate, nitrate, ORP, pH should be considered. If significant variability is found within the area of groundwater contamination, the plume may be subdivided into different portions and differing technologies may be applied.

ORP, pH, nitrate, and sulfate information is used to help focus on which technology is more suitable with the underlying intention of enhancing existing conditions rather than attempting to make dramatic changes in aquifer chemistry. If a plume can be separated into two or more areas based on significantly differing chemistries, it may be possible to select different remedies for differing portions of the plume.

OTHER CONSIDERATIONS

The decision tree does not address the effect of the occurrence of clay or sand (geologic) or permeability limitations on these technologies. Such issues are best evaluated on a site-specific basis. In general, technologies that require injection or extraction tend to be limited by variations in permeability, and some of the thermal technologies may perform better when conductive material (ie, clay) is present in the subsurface. A site specific determination of the effects of the site geology on potential performance of a selected remedial technology is recommended but is not covered in this document.

Pilot studies are helpful in confirming the effectiveness of a given technology. They also may aid in remedial design and in cost estimation. Information regarding recommended objectives for pilot studies is included near the end of this document (p.11). For larger plumes, a pilot study is very helpful in confirming the appropriateness of the technology selection. This decision tree is best used in conjunction with a pilot study to select a final remedy for a site.

After a technology has been selected and implemented at a site, review of the technology's effectiveness should occur on an annual basis. The Department also recommends a detailed review and evaluation after five years to determine if any new technologies have been developed that may assist in remediation, and to evaluate any changes in standards or receptor endpoints that may affect the continuation or applicability of the remedy. Water quality monitoring parameters that are helpful for evaluating remediation performance are included on tables at the end of this document.

This Chlorinated Solvent Decision Tree is not an enforceable document. It has been developed for educational and practical purposes to streamline remedy selection for chlorinated solvents.

Brief Synopsis of Technologies Included in the Decision Tree

Air Sparging: Injection of air into the subsurface to transfer contamination from the groundwater into vapor form. Injection should be performed in conjunction with soil vapor extraction to control migration of contamination in vapor phase and to control indoor air issues, if pertinent. Addition of heat through steam injection is considered an enhancement of this technology.

ERD: Enhanced Reductive Dechlorination. Creation of reducing conditions by injection of various substrates into the aquifer may stimulate biological activity allowing chlorinated solvents to be reduced or degraded to harmless by-products depending on the ambient subsurface geochemistry within the area of groundwater contamination. Bioaugmentation is an enhancement of this groundwater remediation alternative.

ISCO: In-Situ Chemical Oxidation. Consists of injection of various liquid or gas amendments to destroy contaminants in place. Sometimes requires soil vapor extraction to prevent migration of contamination outside the treatment area and to control indoor air issues, if pertinent.

MNA: Monitored Natural Attenuation. Based on dilution, dispersion, and degradation, it is possible that an area of groundwater contamination may reach remedial goals over a period of time without any treatment of the ambient groundwater. MNA may be appropriate for plumes with low levels of contamination provided the plume is stable or decreasing based on adequate monitoring, the time frame to reach remedial goals is reasonable, and impact of a surface water body or receptor above applicable standards does not occur. Understanding of the fate and transport of contaminants in groundwater at the site is an essential component of MNA.

Phytoremediation (Phyto): In the context of this document, phytoremediation refers to the use of plants or trees to extract contaminated groundwater from the subsurface. Seasonality should be considered as part of the selection and design process. Phyto is applicable if contamination is relatively shallow and not toxic to the vegetation being used.

Thermal: Includes electrical resistance heating (ERH) and thermal wells. These technologies heat up the subsurface and either volatilize (ERH and thermal wells) or destroy (thermal wells) contamination. These technologies require soil vapor extraction to prevent migration of contamination outside the treatment area.

ZVI: Zero-valent iron. This results in removal of chlorine molecules from chlorinated solvents eventually forming harmless byproducts In this document, particle size and methods of emplacement are not discussed; simply effectiveness and time frames associated with the technology are considered.

Other Frequently Used Acronyms DRAFT

MCL: Maximum Contaminant Level

ORP: Oxidation/Reduction Potential measured in a flow-through cell in the field during groundwater sampling.

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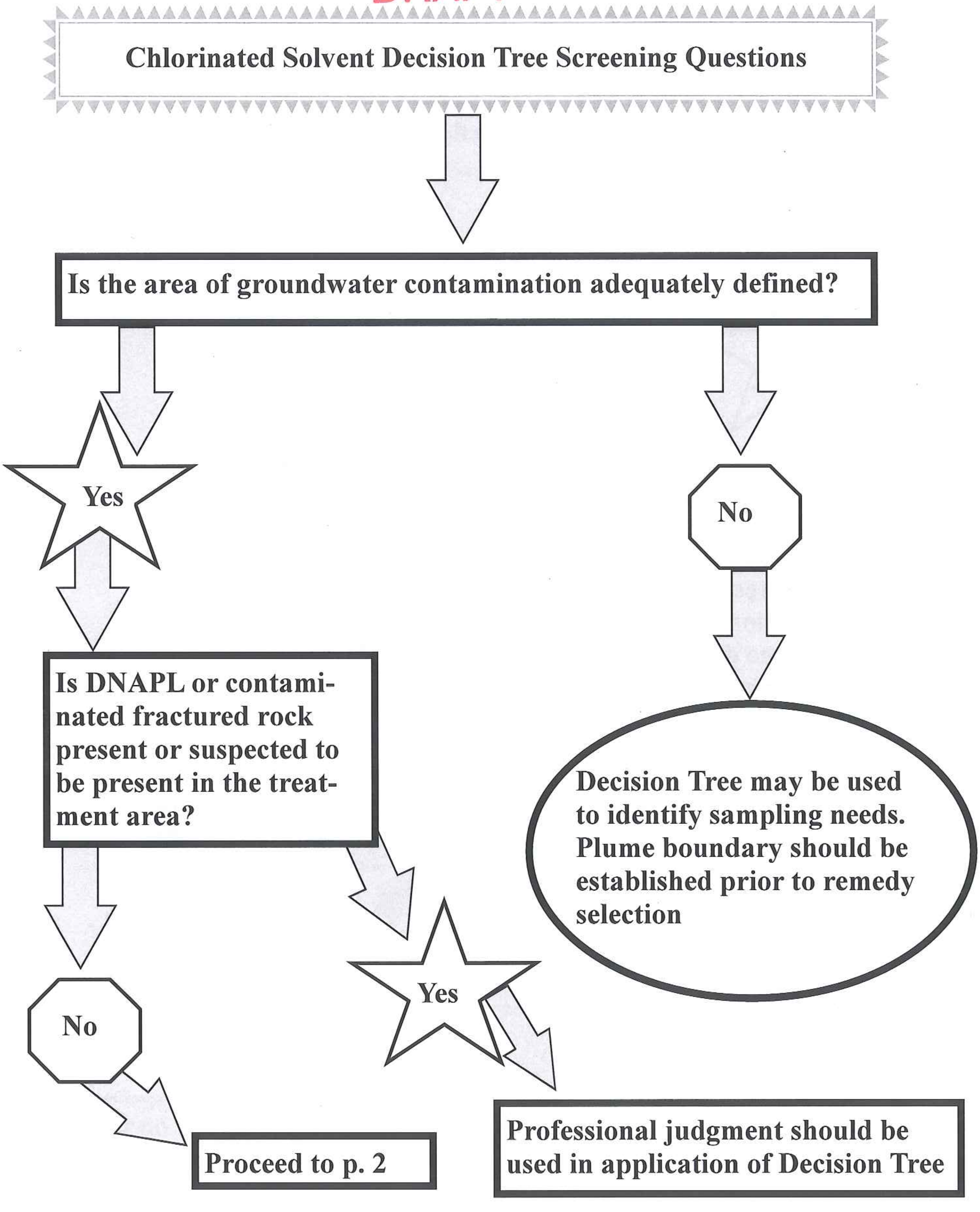
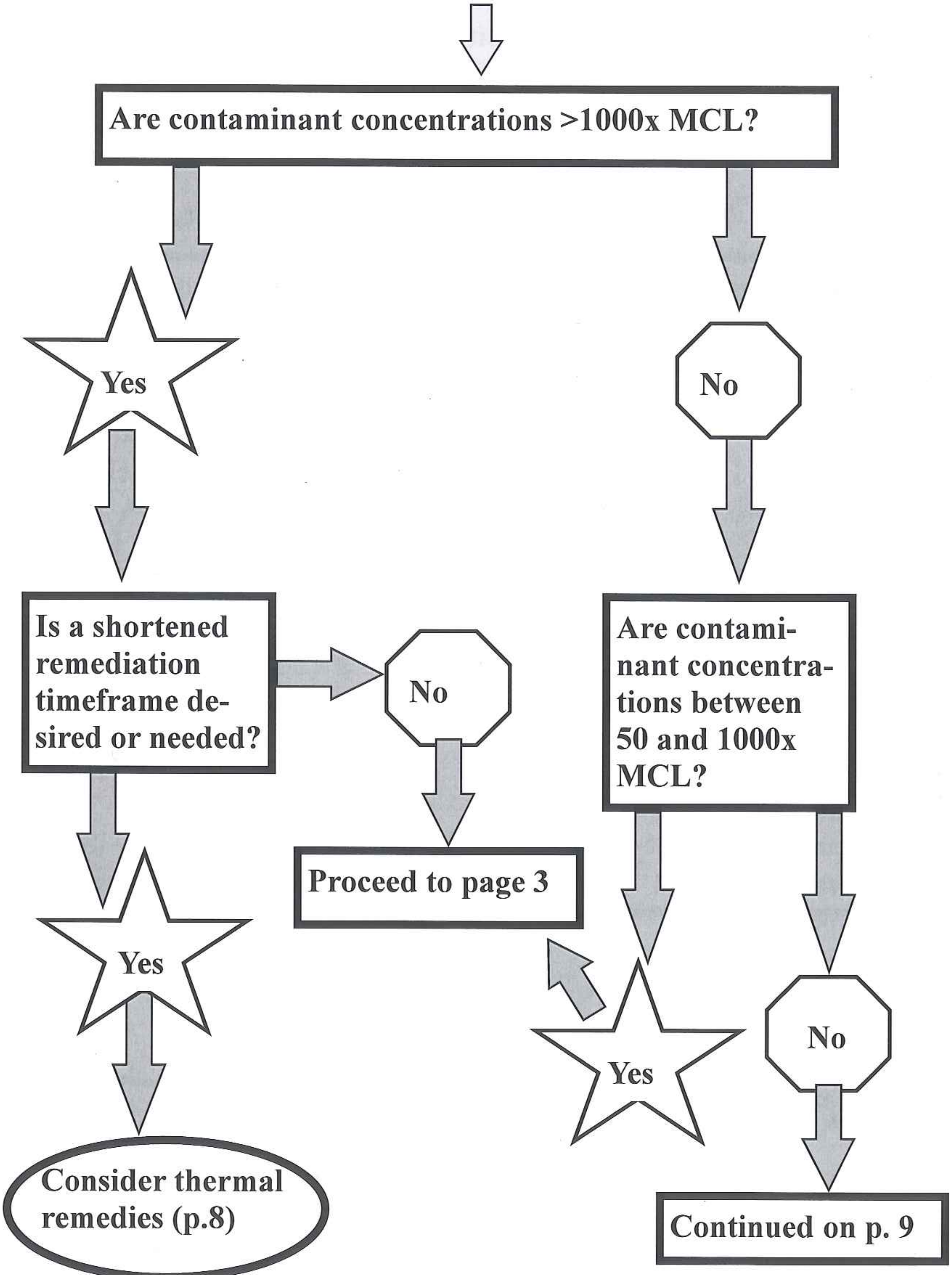
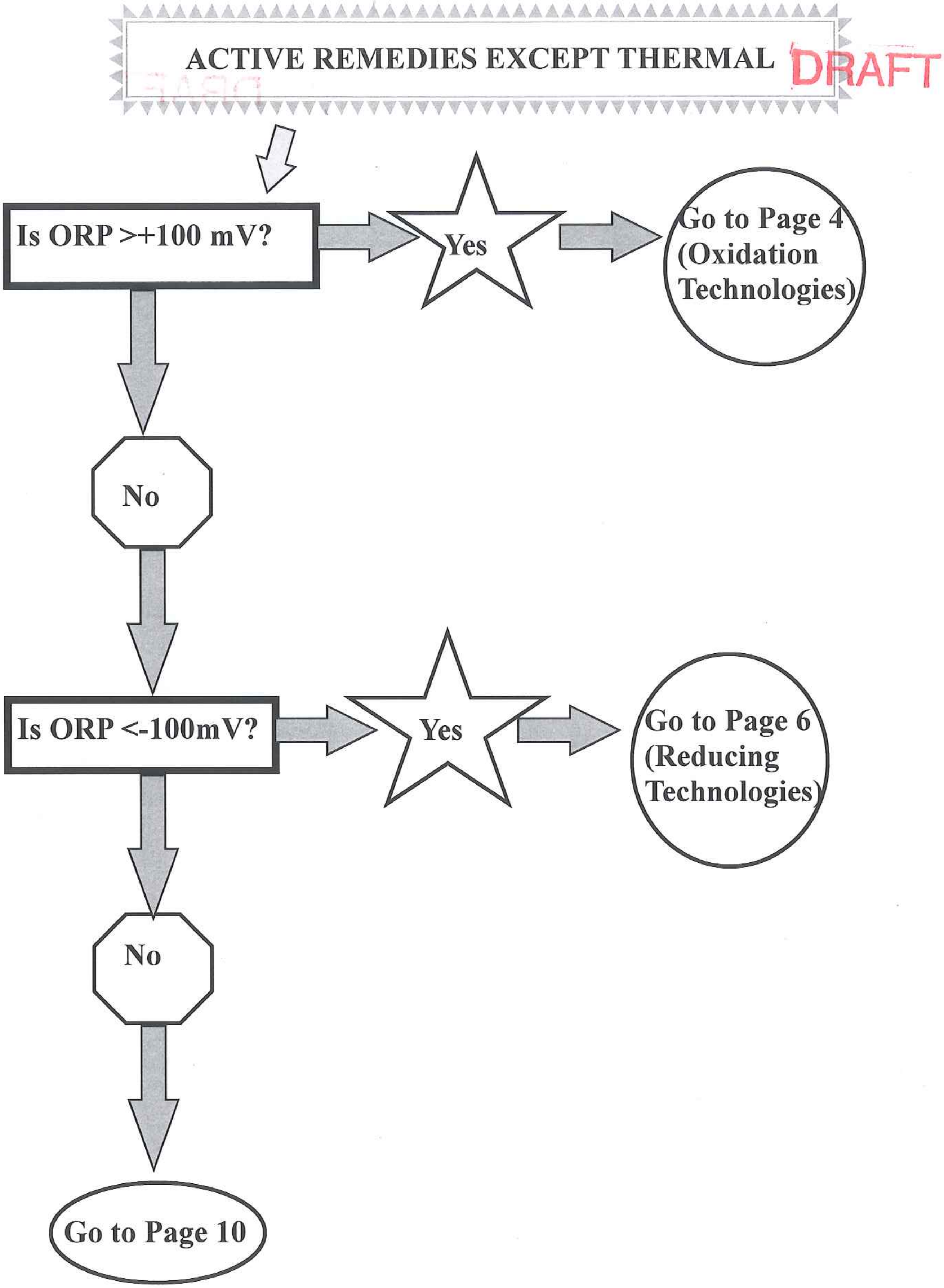

Chlorinated Solvent Decision Tree Screening Questions
Is the area of groundwater contamination adequately defined?
Yes
No
Is DNAPL or contaminated fractured rock present or suspected to be present in the treatment area?
Decision Tree may be used to identify sampling needs. Plume boundary should be established prior to remedy selection
No
Yes
Proceed to p. 2
Professional judgment should be used in application of Decision Tree

General Technology Selection Decision Tree




ACTIVE REMEDIES EXCEPT THERMAL
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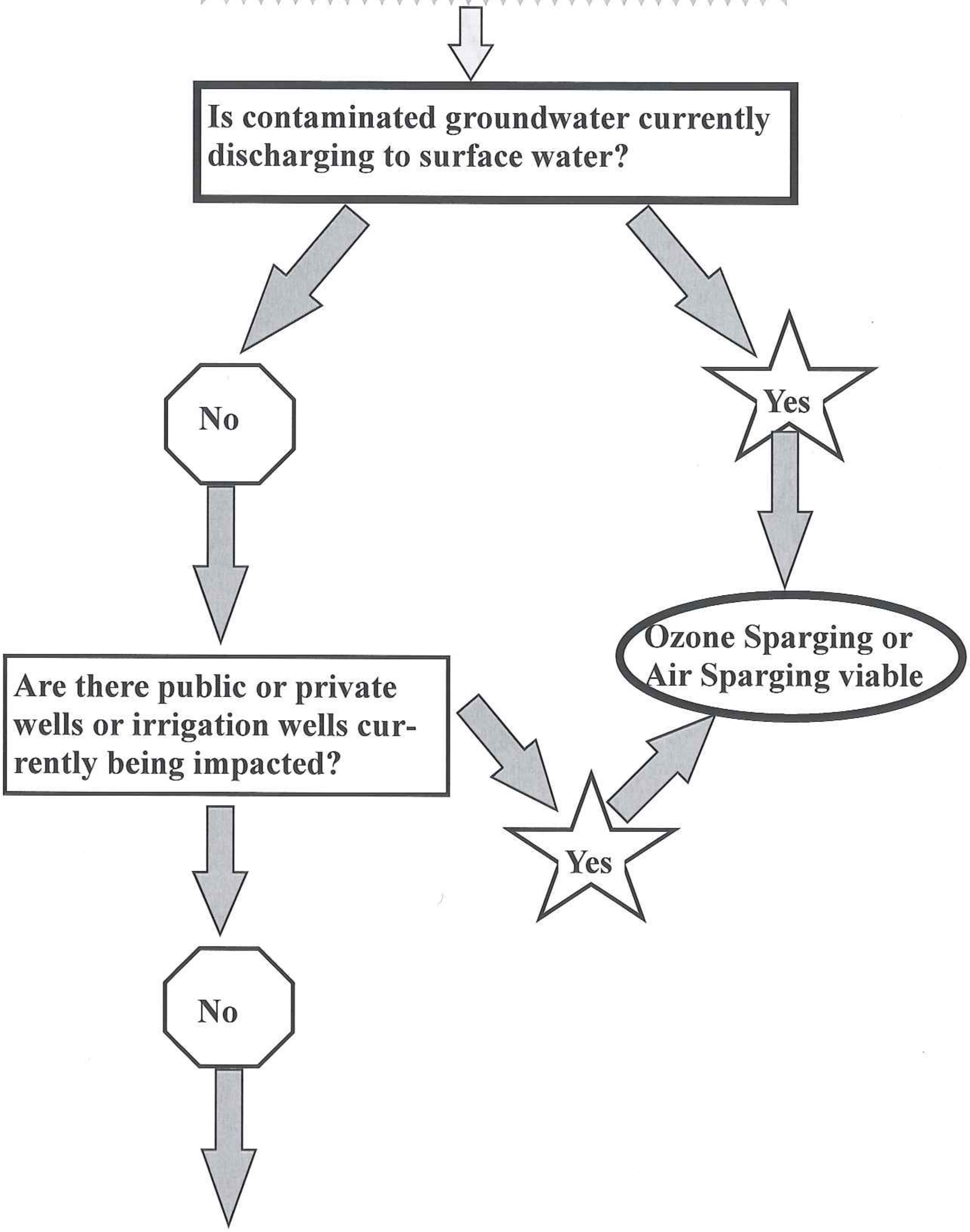
Is ORP >+100 mV?
Yes
Go to Page 4 (Oxidation Technologies)
No
Is ORP <-100mV?
Yes
Go to Page 6 (Reducing Technologies)
No
Go to Page 10

OXIDATION REMEDIES



Go to page 5

OXIDATION REMEDIES
continued from p.4

Is there a potential for contaminated groundwater to enter surface water, a private or public well, or an irrigation well?

No

ISCO should be considered. Ozone, permanganate, Fenton's persulfate,and other amendments available; pilot or bench-scale study may be performed to help select Amendment (p. 11)

Yes

Ozone Sparging and Ai Sparging are viable options. ISCO may be considered with evaluation of travel times to nearest receptor and amendment longevity. Bench scale and pilot scale testing recommended to confirm longevity and effectiveness of amendment. Go to p. 11

REDUCING REMEDIES

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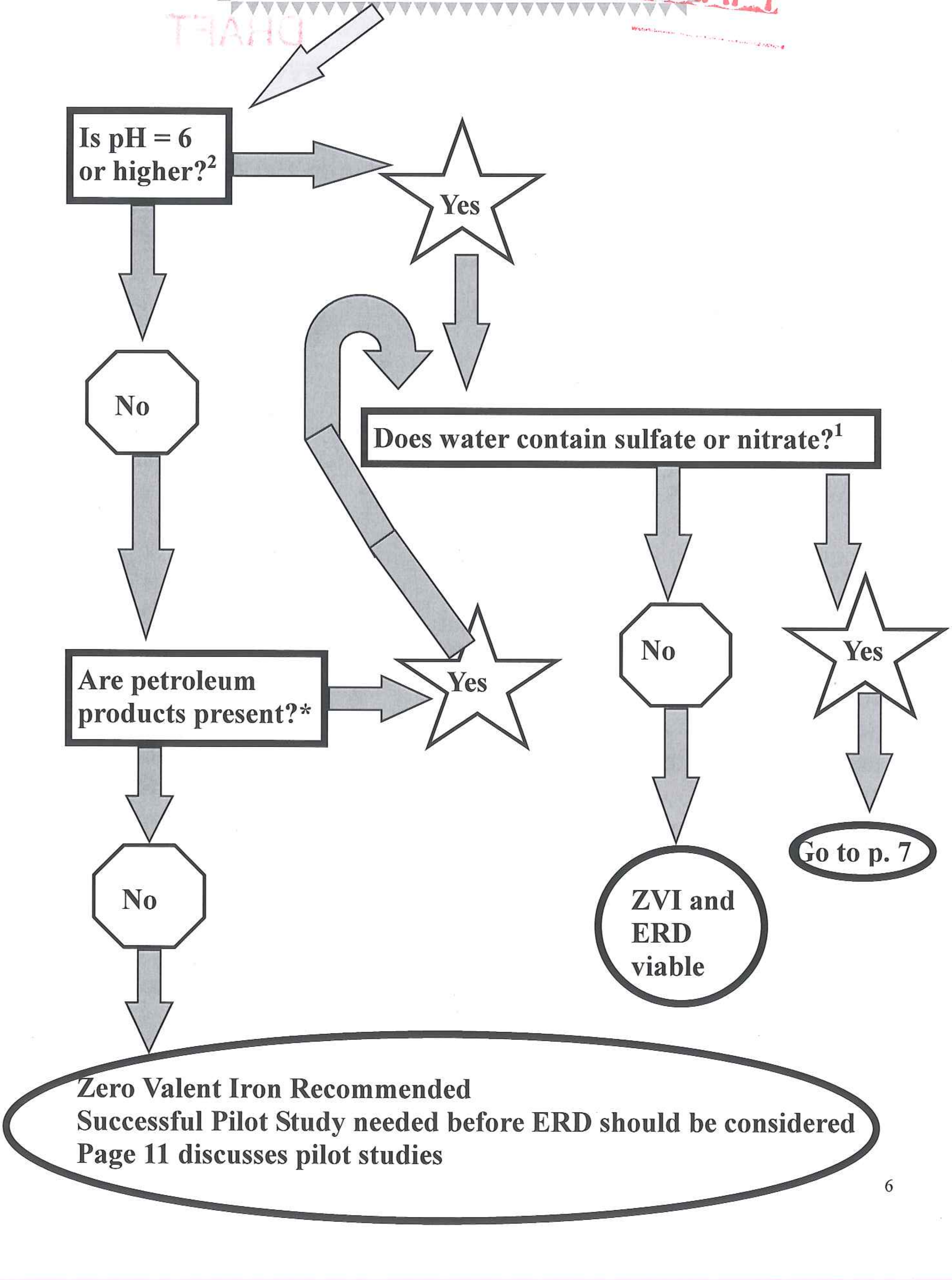

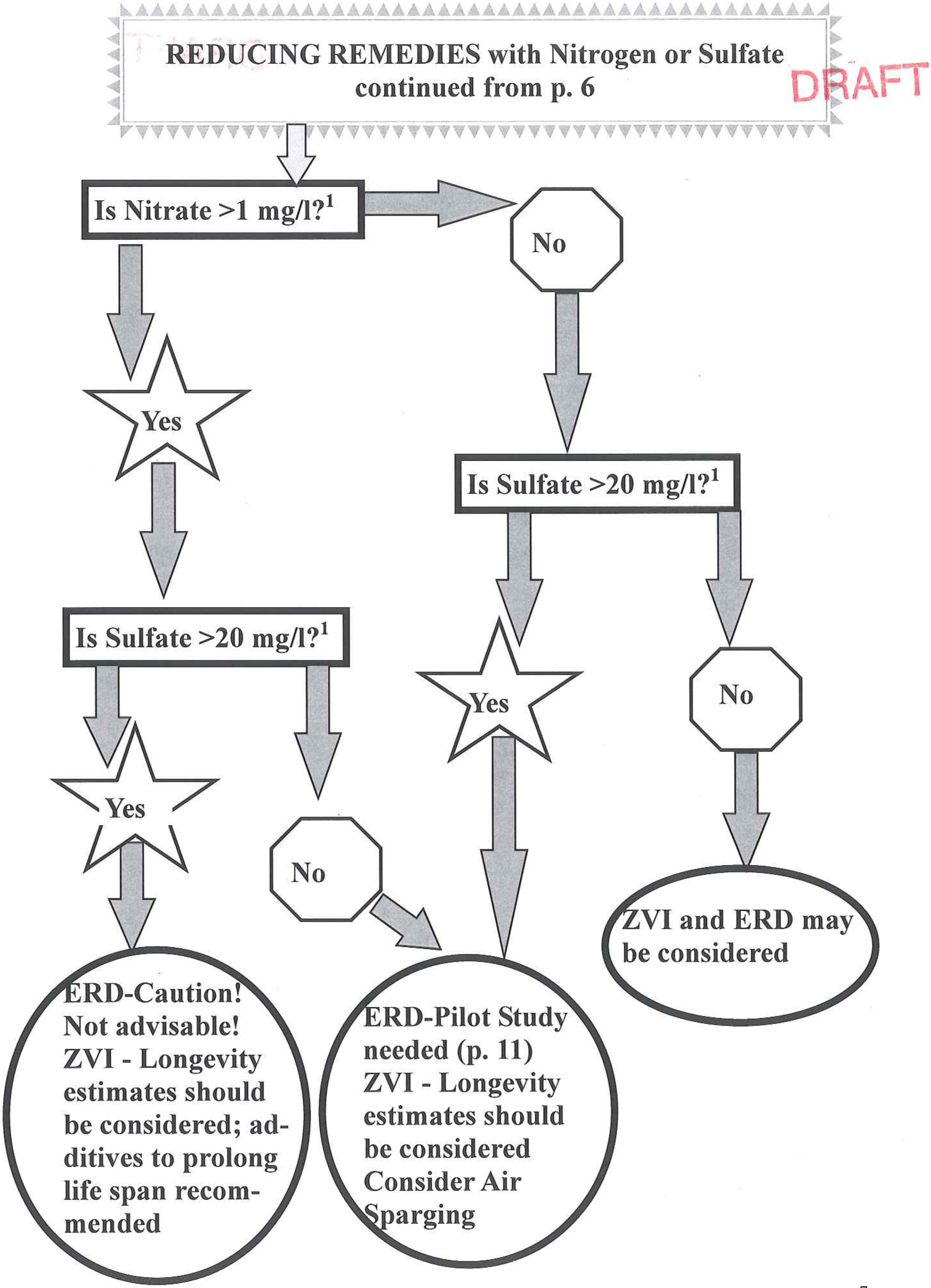
REDUCING REMEDIES with Nitrogen or Sulfate
continued from p. 6
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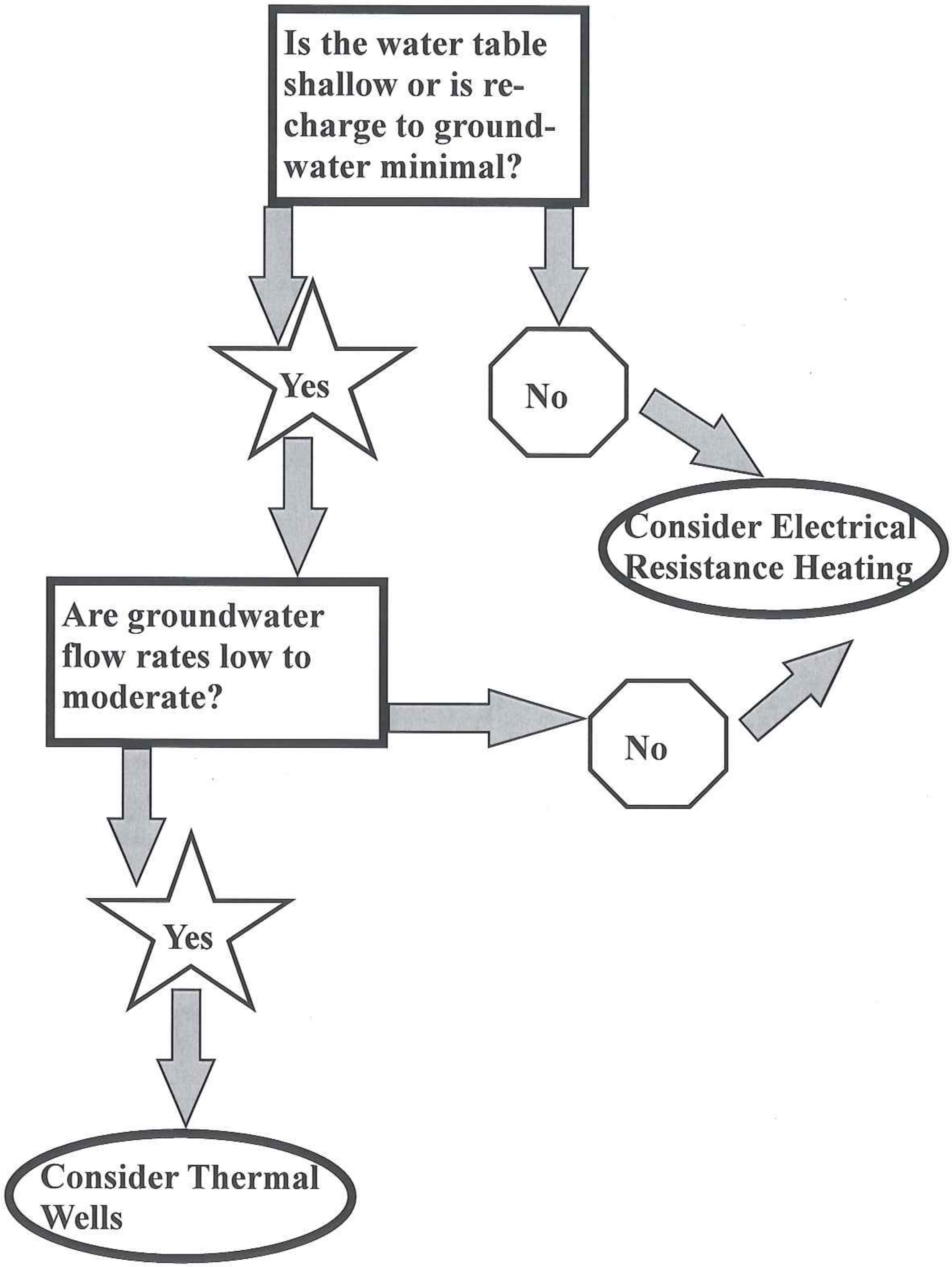
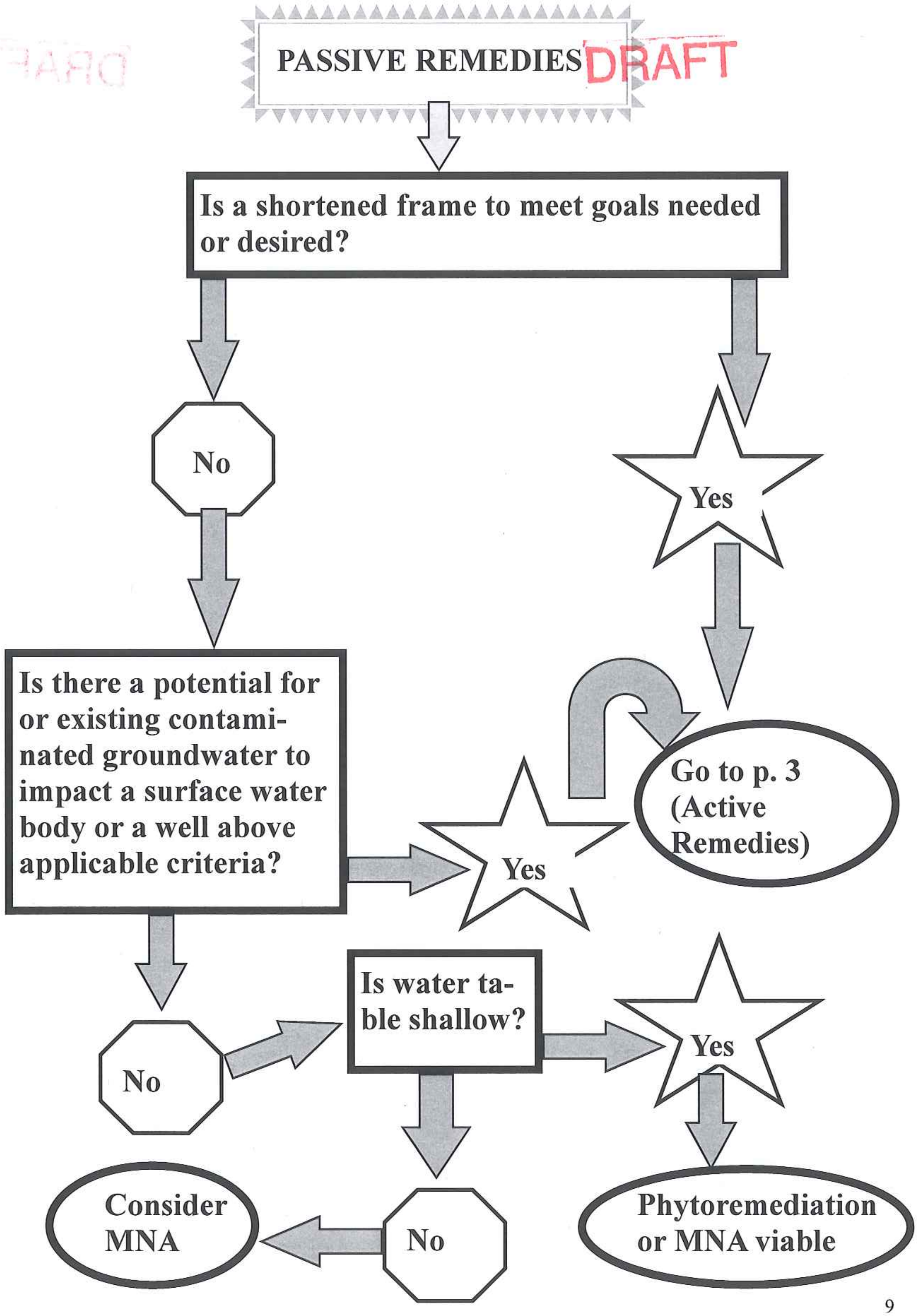
Is Nitrate >1 mg/l?[1]
No
Yes
Is Sulfate >20 mg/l?[1]
Is Sulfate >20 mg/l?[1]
Yes
No
Yes
No
ZVI and ERD may be considered
ERD-Caution! Not advisable! ZVI - Longevity estimates should be considered; additives to prolong life span recommended
ERD-Pilot Study needed (p. 11) ZVI - Longevity estimates should be considered Consider Air Sparging

Note: Site specific evaluation of geology recommended to confirm selection of type of thermal method




PASSIVE REMEDIES
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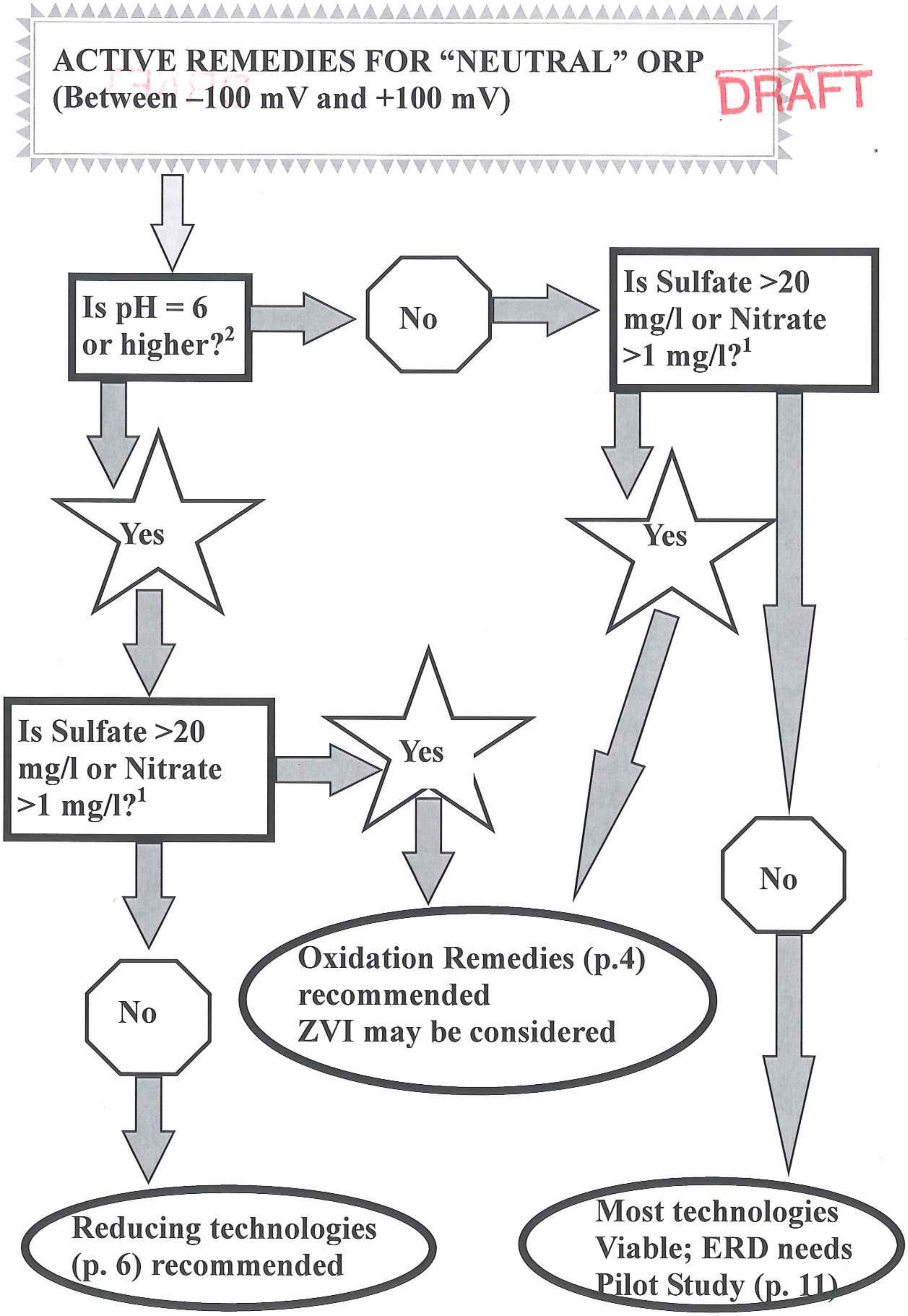
Is a shortened frame to meet goals needed or desired?
No
Yes
Is there a potential for or existing contaminated groundwater to impact a surface water body or a well above applicable criteria?
Yes
Go to p. 3 (Active Remedies)
No
Is water table shallow?
Yes
No
Consider MNA
Phytoremediation or MNA viable


ACTIVE REMEDIES FOR "NEUTRAL" ORP
(Between –100 mV and +100 mV)
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Is pH = 6 or higher?²
No
Is Sulfate >20 mg/l or Nitrate >1 mg/l?¹
Yes
Yes
Is Sulfate >20 mg/l or Nitrate >1 mg/l?¹
Yes
No
Oxidation Remedies (p.4) recommended
ZVI may be considered
No
Reducing technologies (p. 6) recommended
Most technologies Viable; ERD needs Pilot Study (p. 11)

Pilot Study Guidelines
Continued from p. 11

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C. Oxidizing Remedies (ISCO)

-How much amendment is required to achieve goals?
-What is the effect of the natural oxidant demand on performance?
-Does the amendment successfully raise the ORP?
-What is the estimated length of time required to meet remedial goals based on the results of the pilot study?

II. Pilot Study Design Issues

A. Ideal Location and Size of Pilot Study Area

-Typical hydrogeology for site
-Not likely to be impacted by upgradient source
-Typical contaminant concentrations
-Sufficient existing well coverage if possible
-Large enough to be meaningful
-Small enough to be cost effective

B. Ideal Length of Pilot Study

-6-12 months
-Option to extend if needed
-May need to be longer for ERD to detect cis-DCE stall

C. Ideal Monitoring Plan

-Sufficient sampling frequency
    -baseline essential
    -recommend initial weekly to monthly
    -quarterly for extended monitoring
-Sufficient length to detect rebound
-Dilution evaluation
-Cosolvency issues
-Plume mobilization
-Sufficient number and location of properly screened wells
-Sample for COCs, indicator parameters (p. 13), process parameters, byproducts (p. 14), daughter products

Pilot Study Guidelines

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I. Define Objectives

A. All Injection Technologies

-How much injectate can be received in a single point at one time?
-What is the radius of influence?
-What is the longevity of the injectate after it enters the subsurface?
-If multiple/continuous injections are planned in a single location, does well fouling or clogging reduce the amount of injectate a well can receive during the second and subse-quent injections?
-What is the effect of mounding of the water table?
-Are unwanted byproducts formed?
-Any health and safety limitations?

B. Reducing Remedies (ERD)

-How much amendment is required to achieve goals?
-Is the bacterial population suitable for ERD?
-Does the amendment successfully lower the ORP?
-Are volatile fatty acids being formed as a result of injection?
-Are parent compounds decreasing and daughter products increasing after injection?
-Is ethene being produced?
-Is cis-1,2-DCE converting to vinyl chloride?
-What is the estimated length of time required to meet remedial goals based on the results of the pilot study?

Note: The length of time an ERD pilot study is conducted may be critical in accurately predicting success and time frames. Studies should be long enough to determine if there is a cis-1,2-DCE stall or if vinyl chloride and significant amounts of ethene are produced.

Indicator Parameters For Water Quality Monitoring

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Technology	DO	ORP	TOC	pH
ERD	*	*	*	*
ISCO	*	*	*	*
PRB	?	*	?	*
ISCR	*	*		
ORC	*			
Thermal				
Phyto	*			
Air Sparging	*	*	*	*
Pump and Treat	*	*	*	*

*= yes; ? = maybe

Process and Byproduct Parameters For Water Quality Monitoring

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	Volatile Fatty Acids	Dissolved metals	SO_4	NO_3	Alkalin-ity	Microbial Enumeration
ERD	*	*	*	*		*
ISCO		*	*		*	
ISCR		*			*	
ZVI		*				

*= yes;

Footnote and References

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*** Pilot study recommended. If petroleum product is present and pH is less than 6, an extended pilot study is recommended before ERD is selected to determine if ethene is produced[1]**

[1]USEPA, ORD, 1998: Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water. EPA/600/R9-8/128

[2]Robinson, et. al, 2009: pH control for enhanced reductive bioremediation of chlorinated solvent source zones. Science of the Total Environment, v. 407, p. 4560-4573.